CHAPTER 2

LITERATURE REVIEW

The objective of the study is to produce the activated carbon form waste plastics that can be used especially to remove different textile dye molecules from aqueous solution. This chapter demonstrates a review on the pertinent literature which provides a possible maximum input on

1. The types of waste plastics, pyrolysis, characterization and utilization of activated carbon etc.,

2. Various surface properties that signifies the development of porous structure and the methodology adopted

3. Dyestuffs, utilization pollution, treatment options etc., and

4. The overall parameters which influence dye adsorption on activated carbon

The plastic a polymeric material has become the integral part of everybody in the present world. It has replaced many engineering structural materials. It is used from lower end like polyethylene bags to higher end uses like spacecrafts. It’s being used in large quantities and growth rate is increasing every year to meet various consumer demands and technology development. Highest portion of solid waste plastics have been subjected land filling, however, land fill is raising costs, generating greenhouse gases and poor biodegradability. The usage and disposal are diverse and include accumulation of plastics waste in landfills generating a major health and environmental problem for living organisms (Thompson et al. 2009).
Mechanical recycling is reprocessing of waste plastics to new products and has less performance level than the original products. However, the economic viability and practicability of this process in industrial application is not apparent (Mantia 2002). Cleetus is reported pyrolysis process breakdown the long polymer chains into smaller molecular weight compounds and the products are utilized as useful fuels (oil and gases), carbon char and chemicals (Cleetus et al. 2013).

Thermal Pyrolysis processes consists thermal degradation of plastic wastes in N₂ atmosphere to recover the oil, char, combustible gases and tar. Char can be converted into value added materials such as carbon, which is considered to be one of the most environment friendly ways for recycling these types of waste (Gong et al. 2014a, Bernardo et al. 2012, Dias et al. 2007 and Ramos et al. 2009). The use of a catalyst allows modifying the pyrolysis process to produce a narrow molecular weight distribution of hydrocarbon with a higher market value (Marcilla et al. 2009, Lin & Yang 2005). Moreover, the catalyst as case reduces the process temperature, which is an important step in reduction in energy consumption (Lin et al. 2010). The most widely used catalysts are acid solids, such as ZSM-5, USY, SAHA, FCC, MCM-41, HZSM-5, HUSY, HMOR, HY-zeolite, Hβ-zeolite, Mordonite etc., which are selected on the basis of their acid strength and surface characteristics (Lin & Yang 2005, Hernandez et al. 2005). The pyrolysis of different kinds of plastics (LDPE, HDPE, PP,PS, PET, PVC and their mixture) over various catalysts in fixed bed reactors, batch reactors and tubular furnace (Ali et al. 2002, Achilias et al. 2007, Miskolczi et al. 2006, Marcilla et al. 2007, Elordi et al. 2007) were reported.

The solid char is mainly composed of carbon rich matrix that contains most of the inorganic compounds present in the raw wastes and a
significant amount of condensed by-products formed during the pyrolysis process dispersed throughout the solid porous structure. In order to minimize the cost and increase the sustainability of the pyrolysis process, the pyrolytic char should valorised in to possible gaseous and liquid products instead of being directed to landfill disposal. An interesting alternative for the utilisation of char is the valorisation of the char into carbon adsorbent which can be used for pollution abatement. Usually, the pyrolysis chars have porous structures compatible for adsorption purposes (Parra et al. 2002). Due to their potential percentage of fixed carbon and porous structure the solid waste chars are good precursors for preparing activated carbons by means of physicochemical activation (Nakagawa et al. 2004, Morales et al. 2005, Kartel et al. 2006), (Almazan et al. 2007, Garcia et al. 2010).

On physico-chemical activation, the cracking of char increases which in turn increases the surface area of the activated carbon prepared (Tongpoothorn et al. 2011). The surface area of plastic waste activated carbon is good and comparable with other commercial carbon adsorbents (Swiatkowski & Padde 2007, Laszlo et al. 2003). The properties of the final carbon products from a waste plastics precursor can be regulated by using various preparation methods and conditions (carbonization and activation) (Morales et al. 2005, Swiatkowski & Padde 2007).

Depending on the temperature, time of activation and impregnating agent (KOH, H₂SO₄, ZnCl₂, H₃PO₄, steam and CO₂) (Adibfar et al. 2014), pore texture develops by either formation of new pores or widening of existing pores. A waste plastic is one of the most important resources for activated carbon production because of its high adsorption capacity and also due to availability in local communities. The conversion methods of waste plastics into carbon adsorbents depend on the types of plastics.
Activated carbons are porous solids with desirable properties that include high thermal stability, surface area and chemical resistance. High surface area is produced by the numerous pore networks inside the material (McCusker et al. 2003). The present study is pertaining to the preparation of porous carbons from municipal solid waste segregated plastic wastes.

2.1 LOW COST ADSORBENTS FROM PLASTIC WASTE

Lian et al. (2011) studied composition, structure and adsorption behaviour of activated carbon materials prepared from polyethyleneteraphthalate (PET), polyvinylchloride (PVC) and tire rubber (TR) for the removal of methylene blue dye and iodine by highly mesoporous structure. The properties of activated carbon highly depend on their starting polymers and converting synthetic waste polymer into effective adsorbents for environmental remediation and clean up.

Linan et al. (2010) pyrolysed polycarbonate as precursor for activated carbon and used same for the adsorption of methane and hydrogen. The CO$_2$ activation improves mesoporous structure and produces high surface area of the activated carbon as reported by Linan et al. (2010).

Czyzewski et al. (2012) prepared the activated carbon from the mixture of different weight ratios of polyethyleneteraphthalate and magnesium carbonate. The MgO-loaded highly porous carbon materials have more ability to adsorb the two ionic dyes namely reactive red 198 and basic red 18.

The mixed plastics waste such as polystyrene (PS), polypropylene (PP) and polyethylene (PE) are used to prepare the porous carbon nanosheet and used it for the removal of methylene blue from waste water (Gong et al. 2014a). This work is not only provides a novel potential way to utilize waste
plastics, but also puts forward a facile sustainable approach to synthesize porous carbon nanosheet, which are used for dye removal in coloured waste water stream. Gong et al. (2014b) reported cup-stacked carbon nanotubes are prepared by the carbonization of polypropylene (PP) with NiO catalyst. These cup-stacked carbon nanotubes showed high performances in adsorption of heavy metallic ions and organic dyes such as methyl orange, rhodamine B and methylene blue from aqueous solution.

Pyrolysis of plastic waste materials such as polyvinylchloride (PVC), poly urethane (PU) and tire derived rubber particles (TDRP) were used to prepare carbon adsorbent was studied by Elsousys (2013). The adsorption capacity of the carbon produced is explained on the basis of methylene blue number and iodine number.

Adibfar et al. (2014) converted PET wastes into activated carbon through chemical activation with various chemical agents. Usage of low cost, easily available and reproducible raw materials for activated carbon production is of great significance for the economic and environmental view points. The iodine number, methylene blue number and molasses numbers are fixed as standard measures for liquid phase adsorption applications.

Bernardo et al. (2012) studied the char obtained from the pyrolysis of PE, PP and PS plastic wastes and used tires. The quality char was evaluated by some of their physico-chemical properties in order to assess valorisation as adsorbent precursor. The methylene blue adsorption test reveals that adsorptive properties of a carbon material towards a larger molecule to remove organic contaminants from aqueous solution. Since these chars were found to be mesoporous, macroporous materials, they should have good adsorption properties towards bulky molecules like dyes, pesticides etc.
2.1.1 Micro Organisms used as Adsorbents

Various adsorbents are investigated as an alternative to activated carbon. Both living and dead biomass can be used to remove toxic and hazardous organics. (Robinson et al. 2001). Bacteria (Hu 1996), fungi (Kaushik & Malik 2009), yeasts (Safarikova et al. 2005) and algae have been described as good adsorbents (Aksu 2005). Fu & Viraraghavan (2001) reviewed fungal decolourization of dye wastewater; Forgacs et al. (2004) reviewed biodegradation/colourisation potential of bacteria for dye wastewater. Srinivasan and Viraraghavan (Srinivasan & Viraraghavan 2010) reviewed the decolourization of dye wastewaters by bio-adsorbents.

2.1.2 Agricultural Waste used in the Decolourisation of Synthetic Dyes

The abundance and widespread availability of agricultural by-products make them good source of raw materials for dye removal. Several agricultural waste products like rice husks, corncob, coir-pith, plum kernels, bagasse pith, nut shells, used tea leaves, fruit shells, seed husk, leaf powders, fruit peels, saw dust, hyacinth root etc, were tried as alternative and low cost adsorbent by various researchers in recent and past decades. A comprehensive study of the application of bio-adsorption for the removal of organic pollutants found in the reviews by Aksu (2005), Salleh et al. (2011), Sharma et al (2012) and Tripathi (2013). Reviewed literature mainly focus (Sharma et al. 2012)

- to predict the performance of the adsorption processes for dye removal from real industrial effluents under a range of operating conditions
- to better understand adsorption mechanisms.
The removal efficiency of activated carbon prepared from agricultural residues depends on various factors such as surface area, pore structure, nature of charge present, chemical composition and mechanism of adsorption. The removal efficiency also depends upon the characteristics of adsorbate which is to be adsorbed. The characteristics of adsorbate vary with significant variation in concentration, contact time and pH. Adsorption is a complicated process and not accomplished by a specific mechanism. Hence, work is still required to identify the mechanism of adsorption.

2.1.3 Non Conventional Low Cost Activated Carbon Adsorbents from Industrial Wastes

Industrial waste products have also been used extensively by researchers because of its low cost and availability. Fly ash has been used for the removal of dyes (Janos et al. 2003, Dizge et al. 2008). Various types of industrial wastes such as carbon slurries (generated in fertilizer plants), blast furnace slag (generated in steel plants), dust and sludge obtained from steel industries was investigated as adsorbents (Gupta et al. 2003). Lanlan Yu & Qin Zhong (2006) studied the carbon containing adsorbents which were made from biochemical and surplus sludge obtained from different plants by physical and chemical activation for the waste water treatment. Natural coal (Mittal & Venkobachar 1993) and activated bleaching earth (Tsai 2004) are also studied by the researchers as low cost adsorbents used for the decolourisation of dyes.

Many efforts have been made to produce activated carbons from a various residues such as waste newspaper (Okada et al. 2003), charred plant material, graphite, petroleum wastes, sewage sludge (Crini2006), plastic waste (Bratek et al. 2013, Bernardo et al. 2012 & Bazargan et al. 2013) and

The objective of this dissertation is to report the results of the feasibility study utilizing plastic waste activated carbon (after carbonization), as adsorbent to common different classes of dyes namely acid, basic, direct and reactive. Adsorption kinetics of dyes by the adsorbents and regeneration of adsorbate and adsorbent have been focused out. Since the selected adsorbent being a plastic solid waste, utilization of them as adsorbent may provide an effective solution for effective municipal solid waste management. The study using the above said adsorbent is expected to be economical, environmentally safe and of practical importance.

2.2 SOURCES OF DYE WASTEWATER

Due to rapid growth in population and change in life style the demand for the fabrics continue to grow. Humans are aware about the importance of colour fabrics in their day-to-day life. These forces the textile manufacturer’s to colour the fabrics using different dyes. Colour intensity and high resistance to light, washing and perspiration are special requirement for the textile industry. As a result, modern textile dyes are required to have a high degree of chemical and photolytic stability to keep their structure and colour. As a consequence, one of the major problems the textile dyeing and printing industries is facing the discharge of huge volumes of intensive coloured wastewater. Textile dyes are generally synthetic aromatic compounds, some may embedded with heavy metals in their structure, extensively used in leather, textile and printing industries (Mckay et al. 1999).
Based on chemical composition, dyes are grouped into nitro dyes, diphenylamine dyes, xanthene dyes, phthalein dyes, anthraquinone dyes, azo dyes, heterocyclic dyes and indigo dyes. Based on application, they are classified as acid dyes, basic dyes, direct dyes, reactive dyes, vat dyes, sulphur dyes, pigment dyes, mordant dyes, etc. Dyes are the most important class of water pollutants emanated from textile as well as from dye manufacturing industries. The complex aromatic framework of dyes and presence of heavy metals induce toxicity in dyes even in low concentrations (Gumel et al. 2015).

Increase in textile production, which would lead to deterioration of aesthetic value of the environment (Verma & Ghaly 2008). Current conventional processes sometimes also lead to formation of derivative compounds due to reduction under anaerobic conditions, which could pose more severe hazard in contrast to original dye (Kirk Othomer 1993).

The annual production of dyestuffs are about 6,40,000 tonnes, of which in the textile sector, an estimated 10 to 12 % is lost in residual liquors along incomplete exhaustion and washing processes. Effluent treatment processes for dye containing effluents are currently capable of removing about half of the lost 94,000 tonnes (Albanis et al. 2000). Therefore about 47,000 tonnes per year or 128 tonnes daily find its way into the environment, primarily dissolved or suspended in water (McKay 1982).

For dyeing 1 kg of cotton with reactive dyes requires an average of 70-150 L water, 0.6 kg NaCl and 40 gm reactive dye (Allegre et al. 2006). For processing 1 kg of textile fabric, approximately, 10-300 litres of water is required depending upon the type of fabrics and processing method (Lal 1998). Textile mills engaged in dyeing and finishing of the textile products
and dye manufacturing industries are the main sources of discharge of highly coloured wastewater (Dutta 1994).

2.3 CHARACTERISTICS OF DYE HOUSE EFFLUENT

The effluent from dye industries contains a mixture of all the chemicals used in the dyeing process in addition to the materials derived from the fabric/fibre or yarn being dyed. For cotton dyeing small fibres of cotton are detached from the fabric during scouring/bleaching, dyeing and washing stages. During the scouring and bleaching process some components of the cotton fibres such as pectin, waxes and oils are also dissolved and dirt contaminants are released. So the effluent from a dyeing unit also contains sizing agents, cellulose and synthetic fibres, synthetic dyes, common salt, caustic soda and soda ash, sodium sulphate, surfactants, acetic acid from neutralization stages, oxidizing and reducing agents, finishing chemicals and any auxiliaries etc.,

Wastewater generally contains toxic organic and inorganic pollutants. An inorganic pollutant consists of mineral acids, inorganic salts, finely divided metal trace elements, cyanides and organo-metallic compounds. Some of the trace elements play important roles in biological processes, but at higher concentrations, they may be toxic and disturb the biochemical processes and cause hazards (Arivoli et al. 2008). The textile industry has been condemned as being one of the world’s worst offenders in terms of pollution, requires a great amount of two components: water and chemicals.

The water used in textile industry becomes full of chemical additives and is then expelled as wastewater; which in turn pollutes the
environment by the effluents heat by its increased pH and saturated with dyes, deformers, bleaches, detergents, optical brighteners, equalizers and many other chemicals used during the process.

The textile industries are one of the most chemically intensive industries on earth, and the main polluter of clean water. It is typically alkaline and has high biological oxygen demand (BOD) from 80 to 6,000 milligrams per litre (mg/L) and high chemical oxygen demand (COD), which is approximately 2 to 5 times greater than the BOD level. Wastewater also contains solids, oil and other possibly toxic organics, including phenols from dyeing and finishing and halogenated organics from process such as bleaching. The discharge of heavy metals into aquatic ecosystems increases the alkalinity of water (Joshi et al. 2004).

The turbidity and colour along with oil and scum creates an unsightly appearance. The mineral material contains salts and increasing salinity of the water. These effluents are highly different in composition with relatively low biological oxygen demand (BOD) and high chemical oxygen demand (COD) contents (Mantzavinos 2004). The most typical characteristic of textile wastewater is their strong colour is due to residual dyes. With dyeing process, use of dyes, dyeing assistance with water is must and there by generation of unreacted dyes in wastewater, causing disposal problems which leads to pollution (Ashok 2010). A little more than half of the worldwide productions of organic colourants are textile dyes (Zollinger 2003) and each dye class produces a waste with specific characteristics on application.

The use of pigments produces effluents with high amounts of acrylic binders and metals. Many acid dyes contain metals as a part of dye structure. Acid dyes are based on cobalt, chromium, nickel, lead or zinc ions
which are found to be harmful. For example acid black 172 contains toxic chromium ion in its dye structure (Freeman et al. 1995). Another characteristic of textile dye house wastewater is their recalcitrance due to the presence of compounds such as dyes, surfactants and sizing agents as well as their high salinity, high temperature and variable pH (Pekakis et al. 2006).

Wool processing may release bacteria and other pathogens. Pesticides are occasionally used for the preservation of natural fibres and these are transferred to wastewater during washing and scouring operations. The pesticides are used for mothproofing, brominated flame retardants are used for synthetic fabrics and isocyanates are used for lamination (Pollution prevention and abatement 2007). Chlorine bleach is known to be extremely toxic to the environment and to the consumers, yet chlorine based chemicals are still often used to bleach fabrics. Most of the dyes in textile industry wastewater release aromatic amines like benzidine, toluidine etc.

2.4 DYESTUFFS AND ORGANIC POLLUTANTS

Most of the water pollution problems are basically caused by loose legislation on the discharge of industrial waste waters in days gone-by but which is still inherited and needed to deal with every day.

2.4.1 Dyes

One special category of organic pollutants is dyestuffs. A dye can be generally defined as a coloured substance capable of application, in aqueous or non aqueous solution or in aqueous dispersion, to a substrate so that the substrate acquires a coloured appearance. It is estimated that over 50,000 dyes are available commercially (Crini et al. 2006). Coloured organic substances generally impart only a small fraction of the total organic load in
wastewater. However, high degree of colour is easily detectable and detracts from the aesthetic value of rivers and streams. It is a fact that as far as the public is concerned, the removal of colour from waste water is often more important than the removal of the solvable colourless organic substances, which is generally contribute to the major fraction of the biochemical oxygen demand (Robinson 2001).

2.4.2 Classification of Dyes

2.4.2.1 Dyes

The well known system of classification internationally used for dyes is the Colour Index, devised by the Society of Dyers and Colourists, Bradford, England in 1924. This classification of dyes by first assigning each a generic name determined by its application characteristics and assigning a CI constitution number based on its chemical structure if known. Dyes generally can be classified by their chemical structure or application methods (Kirk Othmer 1993). Based on application, the dyes may be divided into seven classes viz., acidic, basic, direct, mordant, vat, reactive, disperse dyes.

2.4.2.2 Acid dyes

Most of the acid dyes have one or two sodium sulphonate (-SO₃Na) groups which are water soluble and capable of bonding with fibres having the cationic sites. They give a wide range of bright colours on textiles mainly for wool, silk and polyurethane fibres especially when monoazo and anthraquinone structures are used (Ko et al. 2002).
2.4.2.3 Basic dyes

These are developed to dye negatively charged acrylic fibres, forming ionic bonds. They owe their name to the presence of aromatic amino (basic) groups and a cationic amino group is present. Generally, they are mainly used in reinforced nylon, polyesters and they have excellent brightness and colour strength, their light fastness is often low (Malik et al. 2007).

2.4.2.3.1 Direct dyes

These are normally used in a neutral or slightly alkaline dye bath or near boiling point, with the addition of either sodium chloride or sodium sulphate. Direct dyes are anionic colourants that have affinity for cellulosic fibres. Direct dyes are used for cotton, paper, leather, wool, silk, rayon and nylon (Venkata Mohan et al. 2002).

2.4.2.3.2 Mordant dyes

These dyes use a polyvalent metal ion (called mordant) to improve the fastness of the dye on the fibre such as light, water and perspiration fastness. The most commonly used mordant dyes have hydroxyl and carboxyl groups. Mordant dyes are used for dyeing cotton and wool (Iqbal et al. 2008).

2.4.2.3.3 Vat dyes

These dyes are water insoluble and fast dyes applied along with strong reducing agents (sodium bisulphite) and alkali to make the dye soluble. The fabric materials is then exposed to air for oxidation. Vat dyes have mainly anthraquinone (82%) or indigoid/thioindigoid (9%) structures and the former having better fastness properties.
2.4.2.4 Reactive dyes

These dyes utilize a chromophore containing a substituent that is directly reacting with the fibre substrate. The covalent bonds that attach reactive dyes to cellulose or protein molecules make it as one of the most permanent dyes. It is relatively easy to use at ambient environment since it is very stable and mainly used to dye cotton, wool and silk (Ayari et al. 2014).

2.4.2.4.1 Disperse dyes

These are water insoluble dyes. Disperse dyes are mainly used in dyeing, printing of polyester and its blended fabrics.

2.5 TOXICITY OF DYESTUFFS AND ORGANIC POLLUTANTS

Dyes have generated much concern regarding its use owing to its toxic effects. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenicity and respiratory toxicity (Srivastava et al. 2004 and Santhy & Selvapathy 2006). Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to heat, light and oxidizing agents (Sun & Yang 2003). In addition to being toxic, dye effluents may also contain chemicals and it is hazardous for various living organisms (Novotny et al. 2006, Mathur & Bhatnagar 2007, Ratna & Padhi 2012).

Many dyes are made from known carcinogens like benzidine and are also known to accumulate, thus posing a serious threat (Percy 1989). (Umbuzeiro 2005) reported dyes that are known to get reduced to toxic substances inside the living organisms. The genotoxic and cytotoxic effect of dye on human cells has also been studied by Tsuboy et al. (2007). Ratna and Padhi (2012) reported the formation of micronuclei which are formed due to
chromosomal breakage (Clastogenicity) and aneuploidy. They also found DNA in fragmentation due to single and double strand breaks.

2.5.1 Problem Statement

Indian textile Industry is one of the leading textile industries in the world. Indian textile industry largely depends upon the textile manufacturing, export and also plays a major role in the economy of the country. India earns about 27% of its total foreign exchange through textile exports. Further the textile industry of India is also contributing almost 14% of the total industrial production of the country. It is also contributes around 3% to the GDP of the country. Indian textile industry is a largest sector in the country in terms of employment generation. It is not only generating jobs in its own industry, but also opens up scope for the other ancillary sectors. Indian textile industry currently produces employment to more than 35 million people.

Indian dye industries produce different kinds of dyes and pigments. Their production is close to 80,000 tonnes and India is the second major exporter of dye stuffs and intermediates among the developing countries after China (Thiripurasundari et al. 2013). Synthetic dyes is used in the textile and dyeing industries for their ease and cost effectiveness in synthesis, firmness, temperature, high stability to light, microbial attack, detergent and variety in colour compared with natural dyes (Kaushik & Malik 2009).

This has resulted in the discharge of highly coloured effluents that affect water transparency and gas solubility in water bodies. In addition, many dyes are believed to be toxic, carcinogenic (Ratna & Padhi 2012). Over the last decades, the increasing demand for dyes by the textile industry has shown a high potential pollutant. Many dyes are visible in water at concentration as
low as 1 mg L\(^{-1}\). Textile processing wastewater, typically with dye content in the range of 10 to 200 mg L\(^{-1}\), are therefore usually highly coloured and their discharge in water bodies presents an aesthetic problem. As dyes are designed to be chemically and photolytically stable and are highly persistent in natural environment. The release of dyes may therefore present eco-toxic hazard and introduces the potential danger of bio-accumulation that may eventually affect humans by transport through the food chain.

The activated carbon derived from municipal solid waste segregated waste plastic seems to be alternative and environmental friendly method (Ciesińska et al. 2011). The physico-chemical characteristics of the activated carbon produced from plastic waste and its potential on dye removal have been investigated.

2.5.2 Wastewater Pollution Remediation

A proper assessment of any chemical pollution of natural water relies on five elements: (i) knowledge of the type and origin of the pollutants, (ii) the availability of analytical methods for quantification of temporal and spatial variability in concentrations of the chemicals present, (iii) a profound understanding of the processes determining the transport and fate of the chemicals in the system considered, (iv) mathematical transport and fate models of appropriate complexity to design optimal sampling strategies and to predict future developments of a given pollution case and (v) methods for quantification of adverse effects of the chemicals on aquatic life and human health. Notably, the same analytical tools and development knowledge are also pivotal for the design and operation treatment technologies and in situ remediation procedures. In the following, we address some fundamental aspects related to these five elements of an exposure assessment of micro
pollutants. Considering the large number of structurally diverse micro pollutants may undergo numerous interactions with other natural or anthropogenic, dissolved or particulate chemical species and materials. Aquatic micro pollutants are commonly quite challenging tasks and require a broad interdisciplinary approach (Rene et al. 2010).

2.5.3 Technologies for Wastewater Treatment

Despite the development of various technologies for water treatment and reclamation, economic, effective and rapid water treatment at commercial level is still a challenging problem. The systematic approach of water treatment and recycling technologies involves the understanding of the technology that includes construction and operational cost, along with the maintenance and management of removed pollutants. Wastewater treatment and recycling technologies have been classified under the following headings.

i. Primary water treatment technologies
ii. Secondary water treatment technologies
iii. Tertiary water treatment technologies

2.5.4 Primary Water Treatment Technologies

In this category, water is treated at the primary level using screening, filtration, centrifugation, sedimentation, coagulation, gravity and flotation methods. Normally, these methods are used when water is highly polluted. Brief descriptions of these methods are given below.

2.5.4.1 Preliminary treatment

Objective of the preliminary treatment is the removal of the coarse solids and other large materials often found in raw wastewater. Preliminary
treatment processes for dye wastewater include equalization, neutralization and in some cases disinfection. The effluents are not having same concentrations at all the time and the pH will vary time to time. The effluents were stored from 8 to 12 hours in the equalization tank. This will result in a homogenous mixing of effluents and helps in neutralization. Due to frequent change in dyes and conditions in the processing sequence, the effluent pH is liable to vary and it is necessary to neutralize (or) to adjust the pH of the wastewater, depending on the type of treatment process (Keshav 1984).

2.5.4.2 Primary treatment

Objective of the primary treatment is the elimination of settleable organic and inorganic solids by sedimentation method. Approximately 25 to 50% of the incoming biochemical oxygen demand (BOD), 50 to 70% of the total suspended solids and 65% of the oil and grease are removed during primary treatment. Some organic nitrogen, organic phosphorus and heavy metals associated with solids are also removed during primary sedimentation but colloidal and dissolved particles are not affected (Shammas & Wang 2009).

Coagulation/flocculation is a frequently used physicochemical treatment method employed in textile wastewater treatment plants to decolourise textile effluent and reduce the total load of suspensions and organic pollutants (PeiWen et al. 2007). Complete decolourisation of dye wastewater is possible using coagulation/flocculation process (Perkowski & Kos 2002). The main advantage of this method is decolourisation of the textile wastewater that can be achieved through removal of dye molecules from the dye bath effluents, and not by partial decomposition of dyes, it could
produce potentially harmful and toxic aromatic compounds (Golob et al. 2005).

2.5.5 Secondary Treatment

Secondary treatment methods are used to convert the finely divided and dissolved organic matter in wastewater into flocculent settleable organic and inorganic solids (Lakshmana Prabu et al. 2011). Secondary treatment methods, used to reduce organic load of textile effluents known as chemical separation and biological oxidation. The treatment and reuse of industrial wastewater by membrane processes has become more attractive in the last few years due to constraints on water usage (Ismail 2003). Studies have indicated that electro coagulation treatment followed by nano filtration processes were very effective and capable of elevating quality of the treated textile wastewater effluent (Aouni et al. 2009).

Biological treatment process is based on the phenomena of self-purification that exist in nature (Latif et al. 2010). Self purification process is by which an aquatic environment achieves the reestablishment of its original quality after pollution (Ramesh Babu et al. 2007). There are three basic categories of biological treatment aerobic, anaerobic and anoxic (Thomas & Schultz 2005). Anaerobic (without oxygen) and anoxic (oxygen deficient) treatments are similar to aerobic treatment, but the use of micro-organisms that do not require the addition of oxygen.

These micro-organisms use the compounds other than oxygen to catalyze the oxidation of biodegradable organics and other contaminants, resulting in innocuous by-products. In the aerobic system, the free oxygen present in the wastewater will be utilized by the micro-organisms for their
energy requirement, growth, multiplication and existence and in turn CO\textsubscript{2} will be released. The anaerobic process occurs in the absence of free oxygen and converts wastes to methane and carbon dioxide in deep tanks. Sometimes, during the decomposition, it may produce odour problem if the wastewater contains sulphide or sulphate. The foremost commonly used aerobic biological treatment processes are stabilization of ponds, activated sludge, aerated lagoons and trickling filters. The treatment of effluent with azo dyes by both aerobic and anaerobic methodology was reported by O’Neil et al. (2000).

### 2.5.6 Tertiary Treatment

Generally dyes are not biodegradable (Ferrero 2007). Wastewater contains significant quantities of non-biodegradable chemicals and polymeric compounds. The conventional treatment methods are inadequate and there is a need for efficient tertiary treatment process become apparent. Tertiary treatment includes adsorption, ion exchange, reverse osmosis, hyper filtration, oxidation techniques, supercritical water oxidation (Onur & Mesut 2010) etc.

#### 2.5.6.1 Oxidation techniques

A variety of oxidizing agents can be used to decolourise wastewater. Chlorine in the form of sodium hypo chlorite is used to decolourise dye bath effluent (Waters 1984). It is a low cost technique but it has its own disadvantages as it forms absorbable toxic organic halides (AOX’s) (Namboodri et al. 1994). Ozone/Hydrogen Peroxide: Ozone oxidation is a general treatment method for dye degradation because it has been shown to decrease colour, COD of the wastewater (Sukanchan 2010). Ozone decomposition in the aqueous solution gives rise to the formation of peroxide HOO\textsuperscript{-} radicals (Jan & Lech 2003).
2.5.6.2 Electrocoagulation process and foam fractionation

Electrocoagulation is one the effective techniques to remove colour and organic pollutants from wastewater (Holt et al. 2005). Electrocoagulation is an electrochemical method of treating polluted effluent whereby sacrificial anodes (iron or aluminium electrodes) corrode to release active coagulant precursors into the solution (Holt et al. 2005). Foam fractionation is a technique of separation in which a component of the bulk liquid is preferentially adsorbed at the liquid/vapour (L/V) interface and is removed by foaming. Wu et al. (2009) used foam fractionation for the treatment of dye wastewater containing basic violet 5BN.

2.5.6.3 Membrane technologies

Important examples of membrane process applicable to wastewater treatment include reverse osmosis and electro dialysis. Reverse osmosis membranes have a retention rate of 90% or more for the most types of ionic compounds and produce a high quality of permeate (Tinghui et al. 1983, Ghayeny et al. 1998 and Treffry-Goatley et al. 1983). The total dissolved solids from wastewater can be removed by reverse osmosis at different concentration of dyes through aero semi permeable membranes.

Reverse osmosis is suitable for removing ions and larger species from dye bath effluents with high efficiency. Clogging of the membrane by dye molecules after long usage and high capital cost are the main drawbacks of this process (Fahnich et al. 1998). A combination of adsorption and nanofiltration can be used for the treatment of textile dye effluents (Ramesh Babu et al. 2007).
2.5.6.4 **Electrodialysis**

Electrodialysis process is applied to remove salts and ionic substances from solutions (Vera et al. 2004). The dissolved salts (ionic in nature) can be removed by impressing an electrical potential across the water, resulting in the migration of cation and anion to respective electrodes via anionic and cationic permeable membranes.

2.5.6.5 **Electrochemical processes**

The electrochemical treatment of wastewater is examined as one of the advanced oxidation processes, a method of pollution control, offering good colour removal efficiencies. Electrochemical technology is one of the effective methods in many sectors of environmental treatment (Walsh 2001). Electrochemical processes contributes considerable role to environmental control and protection (Maria Jitaru 2007).

2.5.6.6 **Ion exchange method**

Ion exchange can be used for the removal of undesirable anions and cations from wastewater. Ion-exchange is an efficient method, with suitable selectivity since it can not only remove the heavy metal ions but also exchange Ca\(^{2+}\) and Mg\(^{2+}\) ions (Qian et al. 2007). Ion exchange method involves similar passage of wastewater through the beds of ion exchange resins, where some undesirable cations or anions of wastewater get exchanged for sodium or hydrogen ions of the resin.

Kalpana et al. (2007) used titanium phosphate an inorganic ion exchange material as adsorbent for the removal of cationic dyes methylene blue (MB), rhodamine 6G (R6G) and pink FG (PFG). Most of the ion
exchange resins are used in synthetic polymeric materials containing ion groups such as sulphonyl, quaternary ammonium group, etc.

2.5.6.7 Biological degradation

Some selected micro-organisms like bacteria, actinomycetes, yeast and mitosporic fungi are found with ability to decolourise dyes through adsorption (Kátia et al. 2006). The treatment of textile wastewater is purely by biological degradation (microbial degradation) was reported by (Kapdan 2000, Rashmi et al. 2009 and Mutambanengwe et al. 2007). Capalash and Sharma (1992) reported that the degradation of methylene blue in crude extra cellular medium of white rot fungus phanerochaete chrysosporium.

2.5.6.8 Photocatalytic treatment

In this process, when the photoactive catalysts are illuminated with UV light, it generates reactive radical which can decompose organic compounds (Crittenden et al. 1997). The kinetics of azo dye degradation by UV/TiO$_2$ was reported by Tang et al. (1997). However these processes are only effective in wastewater with low concentrations of organic dyes.

2.5.6.9 Adsorption

Adsorption process has been gaining popularity as an effective alternative for separation processes (Wong 2004). Adsorption techniques seem to have the most potential for future use in industrial wastewater treatment (Ncibi et al. 2007). Adsorption is the exchange of material at the interface between two immiscible phases in contact with one another. Adsorption may be either physical or chemical. Adsorption can be explained as, if a solid surface is in contact with a solution, solute molecules from the latter has the tendency to accumulate on the surface of adsorbent as surface
layer. This may be due to the imbalance of surface forces that results in adsorption. Adsorption by porous adsorbents proceeds through the following basic steps (Viajaykumar et al. 2012).

i) Transport of the dye from the bulk to the exterior surface of the adsorbent and adsorption at the exterior surface.

ii) Migration of the dye molecules into the pores of the adsorbent.

iii) Interaction of dye molecules with the available sites on the interior (pores) surfaces, bounding the capillary and pore spaces of the adsorbent.

The rate of adsorption is defined as the rate at which substances are transferred from the liquid phase to the solid phase. The adsorption process is one of the most effective methods for removal of dyes from the waste effluent (Velmurugan et al. 2011).

Weber has identified many advantages of adsorption over many other conventional treatment methods for wastewater treatment (Weber 1978).

These include:

i) Less land area (half to quarter of what is required in biological system)

ii) Not getting affected by toxic chemicals

iii) Greater flexibility in the design and operation, and

iv) Superior removal of organic contaminants.

v) Low cost and simplicity
2.5.6.10 Adsorption and surface complexation

Adsorption is a unique process for the removal of both organics and inorganics from drinking water and wastewater. It is a process by which the concentration of solute is enriched at the surface or interfaces between two phases and provides reliable results without much cost and working efforts.

Adsorption partially restores the balance of forces and is accompanied by decrease in free energy. Adsorption may be classified as physical adsorption, the adsorbate are held on the surface of the adsorbing medium by weak Vander Waals forces, whereas chemisorption involves strong chemical interaction and bonding with the surface of the solid at available active sites. Hence, chemisorption is irreversible.

Adsorption is one of the widely used important unit operations in a number of industrial and natural systems such as, fundamental biological studies, separation and purification processes, recovery of chemical compounds and waste treatment processes (Ranjan Jena et al. 2004).
Adsorption has been found to be superior when compared to other available techniques for waste water treatment in terms of cost, ease of operation, simplicity of design and insensitivity to toxic substances (Mezohegyi et al. 2012).

Adsorption as a treatment process has fascinated considerable attention, since a well designed adsorption system can produce an effluent with virtually no dyestuffs present. McKay et al. (2000) after surveying several textile industries has reported that adsorption using activated carbon has emerged as a practical and economical process compared to other available methods for the removal of colour from textile effluents (McKay et al. 1999). Weber (1978) has identified many advantages of adsorption over other conventional treatment methods for waste water treatment. Adsorption is a surface phenomenon, which includes utilization of surface forces, leading to concentration of materials on the surface of the solid bodies (McKay 1979).

Decolourisation may be a result of two mechanisms: adsorption and ion exchange and influenced by many physicochemical factors, such as dye/adsorbent interaction, adsorbent surface area, contact time, temperature, pH and particle size (Robinson et al. 2001).

It is widely accepted that the dye adsorption process can be represented by four consecutive steps (Al-Godah 2000, Sanghi & Bhattacharya 2002),

1. Diffusion/convection of dye molecules through the bulk of solution

2. Diffusion of dye molecules through a diffusional boundary layer (film diffusion)
3. Diffusion of dye molecules from the surface into the interior of the adsorbent materials

4. Adsorption of dye molecules on the surface of the materials through molecular interactions.

The concentration of the dye and agitation time may affect step 2. Step 3 is usually considered as the rate determining stage which certainly affects the adsorption of adsorbate on the substrate. Step 4 is dependent on the nature of the dye molecules, such as anionic and cationic structures.

It is important to note that step 3 could involve two different phenomena: (1) pore diffusion (adsorbate first diffuses in the liquid, filling the pores and then adsorbed) and (2) surface diffusion (adsorbate is first adsorbed then diffuses from one site to another).

Several adsorbents have been studied to determine their ability to adsorb dyes from aqueous effluents (Oladipo 2013). Amongst all the adsorbent materials proposed, activated carbon is one of the most popular for the removal of pollutants from wastewater (Derbyshire et al. 2001, Ramakrishna & Viraraghavan 1997). In particular, the effectiveness of adsorption on commercial activated carbon (CAC) for removal of a wide variety of dyes from waste water has made it an ideal alternative to other expensive treatment options (Ramakrishna & Viraraghavan 1997).

Higher adsorption capacity of activated carbon than any other material is due to extensive internal porous structure formed during the carbon activation process (Forgacs et al. 2004).
2.6 ACTIVATED CARBON

Activated carbon are carbon that generally have a high surface area and complex pore structure resulting from physical or chemical activation processes. The role of activated carbon, as an adsorbent material to remove pollutants from liquids and from gases is well established by Foo & Hameed (2012) and Mohammed et al. (2014).

Table 2.1 Various adsorbents used for removal of dyes

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyes</td>
<td>Sesame seed pods (Thinakaran et al. 2008), Jatropha curcas L (Revathi et al. 2010), Granular Activated Carbon (Keith et al. 2004), Activated carbon, (Ko et al. 2002), Peat (Ramakrishna and Viraraghavan, 1997).</td>
</tr>
<tr>
<td>Basic dyes</td>
<td>Tuncbilek lignite (Onal et al. 2006), Groundnut shell waste (Malik et al. 2007), Limonia acidissima (wood apple) shell (Ashish Sartape et al. 2014), Bamboo (Hameed &amp; El-Khaiary, 2008), chitin hydrogel (Hu Tang et al. 2012), Moroccan clays (Elmoubarki et al. 2015), Agricultural solid waste (Mohamad Amran Mohd Salleh et al. 2011).</td>
</tr>
<tr>
<td>Direct dyes</td>
<td>Coal based adsorbents (Venkata Mohan et al. 2002), Beech wood sawdust (Dulman and Cucu-Man 2009), Agricultural waste (Bharathi &amp; Ramesh 2013), Carra Sawdust Treated with Formaldehyde (Nedher Sanchez et al. 2012), Starch Composites (Hashem &amp; Abdel-Halim 2007).</td>
</tr>
</tbody>
</table>
According to the report of Roskill (2008), the demand of the activated carbon has been increasing worldwide. They also projected the consumption of activated carbon is slightly over the estimated production in 2007. Growth in consumption of activated carbon in current market is forecast to be 5% per year through 2015 and there will be a continuous increase in demand due to the water and effluent treatment applications to control disinfection by-products in drinking water, and in the industrializing countries to upgrade the quality of drinking and wastewater. Some high carbon content materials have been under investigation as raw materials to prepare activated carbon including industrial, agricultural and domestic wastes and hopefully, the research product could be commercialized in the future.

2.6.1 Removal of Colours from Textile Wastewater- Role of Activated Carbon

The use of activated carbon for textile industrial wastewater is well known for the past half century (Bansal & Goyal 2005). Venkateswara Rao and Sastry (1987) documented the work done by different workers towards the different dye adsorption by commercial activated carbon application.

McKay (1982) studied the ability of activated carbon to remove dyestuffs from aqueous solutions. The range of dyestuffs include acidic, basic, direct and reactive dyes and the effect of several factors on adsorption by activated carbon have been studied, namely, temperature, agitation time, initial dye concentration, adsorbent concentration, adsorbent particle size range, pH of solution and salt concentration. It is also reported that effect of external mass transfer, pore diffusion and intra particle diffusion at the rate of adsorption. Mass transfer effect during colour removal by activated carbon is reported by Ruthyu LiYeh (1995). A film pore double resistance model for
mass transfer is used in this study to determine the effect adsorption diffusivity for the adsorption (McKay 1983). The relationship between saturated adsorption amount, pH, $\zeta$ potentials for different cationic and anionic dyes on activated carbon have been studied by Dai (1998).

2.6.2 Objective of Study

The objectives of this present study are:

1. To develop activated carbon from municipal solid segregated plastic waste using physical activation process.

2. To study the optimum condition (temperature range for pyrolysis process and the quantity of activating agent) of activation process.

3. To characterize the produced activated carbon with suitable methods.

4. To investigate the efficiency of prepared activated carbon towards the adsorption of various classes of dyes namely acid, basic, direct and reactive.

5. To study the effect of various process parameters of adsorption on activated carbon prepared.

2.6.3 Rationale and Significance

This research is done based on the significance of activated carbon production in India. In future, India would be the leading producer of activated carbon from unconventional precursor like plastics waste, agricultural waste and other possible industrial waste residues. The activated
carbon produced from plastics waste is expected to play an important role in the removal of different water polluting contaminants including mutagenic and carcinogenic substance such as phenol, pesticides, insecticides, heavy metals, dyes etc. Hence, this research is expected to benefit the plastic waste management sector and chemical industries to manage their waste disposal in an efficient eco-friendly way. The processing and transformation of plastics waste into activated carbon with better adsorption properties would reduce problems of disposal and management of these waste by-products, while providing a high quality end product for water and wastewater treatment that could potentially expand the carbon market (AlOthman et al. 2011).